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HIGH-TEMPERATURE FRACTURE AND NON-NEWTONIAN FLOW OF GLASS MELTS

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ABSTRACT

Both high-temperature fracture behaviour and non-Newtonian flow of TV glass melts under extreme forming conditions have been studied by means of a parallel-plate compression method. Due to the fluctuation of the glass composition, which is caused by instability of the production process, the viscosity-temperature curves of the two melts slightly deviate from each other. Although the deviation is small, it leads to a relatively big difference in the fracture behaviour of the two melts under the isothermal conditions. However, the non-Newtonian flow behaviour of the melts is not sensitive to the fluctuation of the glass composition at comparable deformation rates. The master curves of viscosity - strain rate relation were constructed with the aid of shift factor, from which a prediction of the rheological properties at the low viscosities is possible.

INTRODUCTION

During the production process of glasses, the stability of chemical composition is prerequisite not only for a good quality of products but also for a high productivity. In order to ensure the stable composition, all the technological parameters of production should strictly be kept constant. In reality, however, it is difficult to keep absolutely stable chemical composition and production conditions, since they are influenced by many factors at one time, such as the instability of the raw material composition, the inhomogeity of both batch and melt, the corrosion of refractory materials, changes of redox state and hydroxyl content, cullet level, unstable fuels and firing parameters, ambient atmosphere [1-5]. Consequently, a fluctuation of the viscosity of glass melts will occurs, which leads to a change of the fracture behaviour or the isothermal workability of glass melts [1] and possibly to a disturbance of forming process. But to avoid the negative influence caused by the fluctuation of viscosity at a given temperature, the technological parameters of forming process has to be steadily adjusted and optimised. To do this, it is necessary to conduct a quantitative study on the dependence of the fracture behaviour of glass melt on the fluctuation of viscosity and the forming rate. This is the purpose of the present work. The emphasis of the present work will be placed on measuring tensile strength, critical deformation rate and rheological properties of high viscous glass melts. As a crucial factor, the non-Newtonian behaviour should be taken into account so as to provide valuable information for making a better design of glass forming process and for getting a better workability of glass melts. The glasses for producing television tubes will be the objects of the present study.

EXPERIMENTAL

The glass melts of this study were directly taken from the production line of television tube at two different time points, which were denoted as melt 1 and 2, respectively. Cylindrical samples were drilled from glass plates by a diamond drill with an inner diameter (*D*) of 10.4 mm which were lapped plan parallel to a height (h_0) of 10.5 mm.

The properties of the glass melts were measured with the cylinder compression method, which is described in detail in Refs. [6-8]. Therefore, only the principle is explained here. The cylindrical glass samples are compressed plane parallel under isothermal conditions (i.e. at constant surrounding temperature during the measurement) within the viscosity range of $\eta_0 = 10^{10}$ and 10^9 Pas. The values of both force and piston displacement were automatically registered by a rapid transient recorder with high time resolution (Kontron, München, Germany). As the deformation rate reaches a certain value for the given deformation degree, $\Delta h/h_0$, where Δh is the deformation of a glass cylinder, the first high-temperature crack occurs at the cylinder surface. This value is termed as the critical deformation rate, $\dot{h}_c$. The first crack was detected with the aid of a stripe of conductive silver lacquer coiled around the glass cylinder. As the first crack appears, the stripe of conductive silver lacquer is broken and by that a jump in electric pressure occurs, which is simultaneously registered by the transient recorder. Thus, the values of the force, the deformation and the deformation rate, at which the first crack appears, could be obtained. The evaluation of original values, the mechanical and thermal corrections were done with an improved computer programme, from which the various rheological, thermal and mechanical data could be acquired.

THEORY

The maximum tensile stress produced by pressing cylindrical sample appears at the equatorial line of the deformed cylinder surface. It is the normal stress in the tangential direction and calculated by the equation [7, 8]:

$$\sigma = F \bullet \frac{2R^2\left[\left(\frac{h_0}{h}\right)^{1.5} - 1\right] + h^2}{V\left[\frac{V}{\pi h^2} + 2h\right]} \tag{1}$$

where *F* is the force applied on the sample, *V* is the volume of the sample, h_0 is the height of the sample before compression, *h* is the height of the sample as function of the time of pressing sample.

The maximum tensile stress leading to the first high-temperature crack, is the tensile strength, σ_{ts}. Usually, σ_{ts} and $\dot{h}_c$ decrease with increasing $\Delta h/h_0$. The dependence of σ_{ts} on $\dot{h}_c$ is approximately fitted by the linear relation [1, 9]:

$$\sigma_{ts} = a + b\,\dot{h}_c \tag{2}$$

where a and b are constants. The critical deformation rate is a major criterion for judging the isokom workability of glass melts [1, 9].

The viscosity is determined by the Gent equation [10], which is valid for non-slip condition at the face area of the glass cylinder:

$$\eta = F / \left[3V\dot{h} \left(\frac{V}{2\pi h^5} + \frac{1}{h^2} \right) \right] \tag{3}$$

The relation between the normalised non-Newtonian viscosity, η_{nN}/η_0, and the normalised deformation rate, $\dot{\varepsilon} = \dot{h}/h$ can satisfactorily be expressed by the equation recently developed in Refs. [11-13]:

$$\frac{\eta_{nN}}{\eta_0} = \frac{\eta_\infty}{\eta_0} + (1 - \frac{\eta_\infty}{\eta_0})\frac{\dot{\varepsilon}_g}{\dot{\varepsilon}}(1 - exp(-\frac{\dot{\varepsilon}}{\dot{\varepsilon}_g})) \tag{4}$$

where η_∞ is the ultimate Binghamian viscosity at very large $\dot{\varepsilon}$-values, η_0 is the Newtonian viscosity and $\dot{\varepsilon}_g$ the flow relaxation rate. The non-Newtonian viscosity, η_{nN}, is obtained by theoretically eliminating the viscous heating effect. Eq. 4 reflects the pure structurally caused non-Newtonian flow behaviour.

On the other hand, the dependence of the normalised actual viscosity, η/η_0, may be described by the following equation [11-13]:

$$\frac{\eta}{\eta_0} = \frac{\eta_{\infty,b}}{\eta_0} + (1 - \frac{\eta_{\infty,b}}{\eta_0})\frac{\dot{\varepsilon}_{g,b}}{\dot{\varepsilon}}(1 - exp(-\frac{\dot{\varepsilon}}{\dot{\varepsilon}_{g,b}})) \tag{5}$$

where the index b indicates the parameters with viscous heating effect. To calculate actual viscosity, η, the viscous heating effect due to dissipation of mechanical energy is not theoretically eliminated. The actual viscosity is an important quantity for studying practical workability because it reflects the real decrease in viscosity.

With the aid of the shift factor, a_T, master curves may be established which are independent of temperature of the glass melts, since the glass melts are "thermorheologically simple" fluids. The shift factor may be calculated by the following equation [14]:

$$a_T = \frac{\eta_0(T) \cdot T_C \cdot \rho(T_C)}{\eta_0(T_C) \cdot T \cdot \rho(T)} \tag{6}$$

where T_c is the glass transition temperature, $\rho(T_c)$ the density at T_g and $\eta_0(T_c)$ the Newtonian viscosity at T_c.

RESULTS AND DISCUSSION

Fig. 1 shows the dependence of viscosity on temperature for the two glass melts. The difference in viscosity of the two melts is still detectable, though the curves are plotted logarithmically. Fig. 2 displays the deviation of the viscosity of melt 1 from that of melt 2. The deviation first decreases with increasing temperature, then reaches the constant of $\Delta\eta_0/\eta_{0melt2}$=15% at the temperature of T=650°C and remains unchanged. In other words, the rate of the decrease of the deviation, i.e. the slope of the curve, $d(\Delta\eta_0/\eta_{0melt1})/dT$, decreases with increasing temperature until it reaches the slope of 0 and then does not change any more. This deviation is attributed to the fluctuation of the composition of the melt, which is related to the instability of production.

Though the fluctuation of the composition is small, as shown in Fig. 3 it could heavily affect the isotherm fracture behaviour which is closely related to the isotherm workability of glass melts (“isotherm” means "at same temperature”). To understand the concept of workability, the readers are referred to Refs. [1, 5, 9]. Fig. 3 indicates that the critical deformation rates of the two melts clearly deviate from each other, i.e., the critical deformation rates of melt 2 are clearly higher than those of melt 1. Obviously, this is related to the following facts. On the one hand, in order that melt 1 and 2 are subject to same tensile stress, the latter needs to be compressed at higher deformation rates than the former, since the viscosity of the latter is lower than that of the former at same temperatures. On the other hand, the difference of the tensile strength of the two melts at same temperatures is so small that it can be neglected. In one word, the difference of the tensile strength is not responsible for the difference in the critical deformation rate of the two melts, but the difference in viscosity is. This suggests that, at the same temperature, melt 1 can be worked faster than melt 2. This also means, if melt 1 is pressed with a deformation rate equal to the critical rate of melt 2, the probability of the occurrence of crack will be lower. Another economically favourable possibility is as follows. If the critical deformation rate of melt 1 is used for forming melt 2, the forming temperature of melt 2 can be lowered to the temperature, at which melt 1 has the same tensile stress as melt 2. This is beneficial to reducing the consumption of energy. To do this, a temperature regulation is necessary. In other words, if the forming speed applied to melt 2 is used for the forming melt 1, the latter will be broken, because the pressure exerted by the machine will lead to a tensile stress which can exceed the tensile strength of the melt.

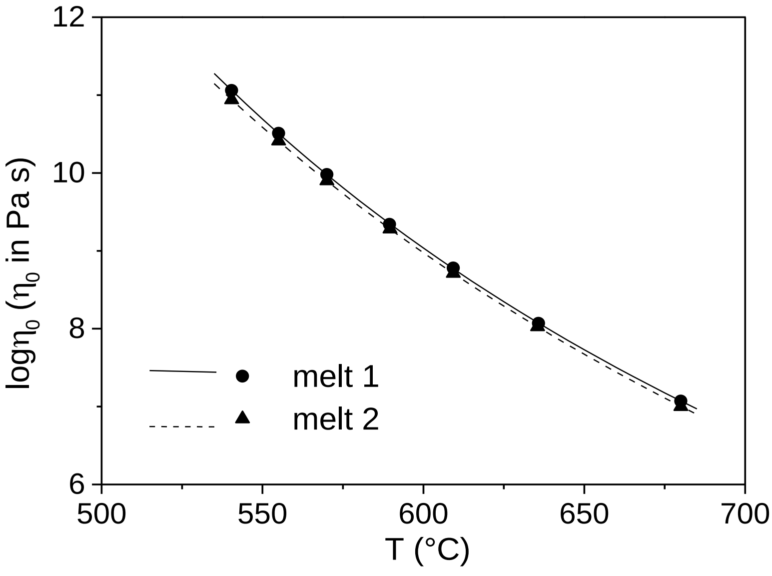

Fig. 1. Viscosity versus temperature for two TV glass melt 1 and 2. The curves were obtained by fitting the measured data with Vogel- Fulcher-Tamman equation.

On the basis of above analysis, in order to optimise the forming process, here exist three possibilities or measures: the regulation of temperature, the control of the forming speed of machine, and stabilisation of the composition of batch. However, before implementing these measures, the economical and ecological benefits should be taken into account.

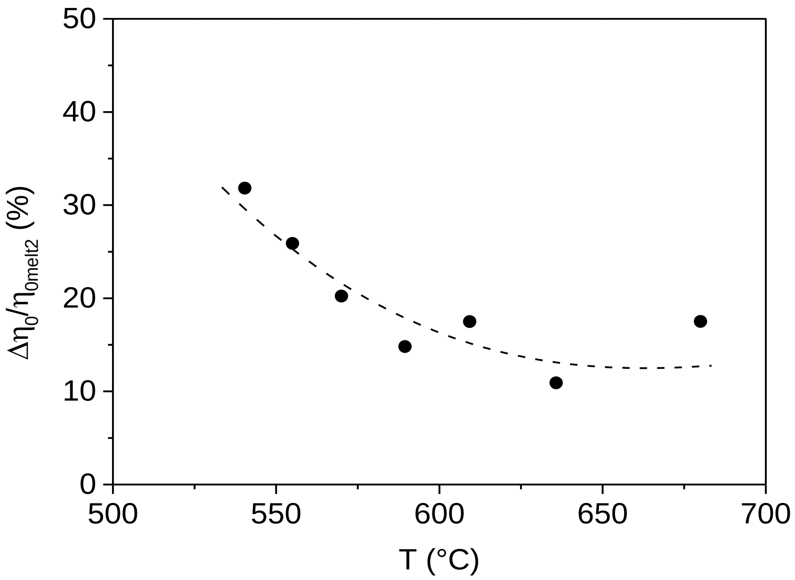

Fig. 2. Deviation of the viscosity of glass melt 1 from that of glass melt 2, $\Delta\eta_0/\eta_{0melt2}$, versus temperature, T.

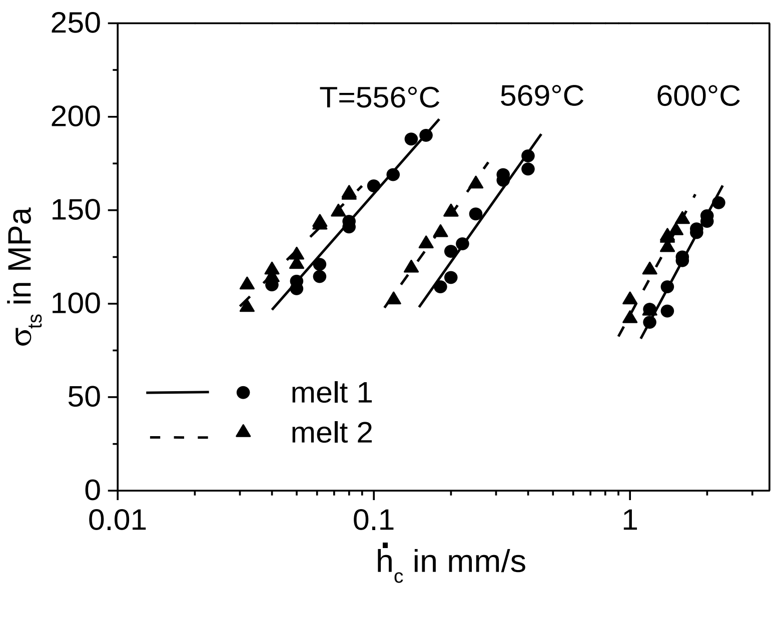

Fig. 3. Tensile strength of glass melts, σ_{ts}, versus the critical deformation rate, $\dot{h}c$, for glass melt 1 and 2 within the deformation range $\Delta h/h0$ = 6 to 30%. The curves were obtained by using Eq. 2

As indicated in Refs. [1-4], the workability of glass melts is affected by the shear thinning flow. If the shear stress applied to a melt is sufficiently high, the shear thinning flow will occur. Usually, the shear thinning flow is favourable to a improvement the workability of glass melts, since it makes possible to raise the forming the speed of glass melts. The concept of shear thinning effect, used in this work, refers to the total effect consistingof two effects: the anisotropic flow and the viscous heating. The viscous heating effect can also lead to broadening of working range of glass melts. Generally, the viscous heating effect is produced by a much lower deformation rate than the one causing the anisotropic flow. Therefore, for relatively low deformation rates, only the viscous heating effect exists and the anisotropic flow does not. However, the occurrence of the viscous heating effect alone could also result in an increase of the critical deformation rate. However, in some circumstances, it could become harmful. For instance, during forming process or drawing process of glass, the shear thinning behaviour of glass melts can cause an uneven distribution of viscosity and temperature in different positions of mould, which leads to an uneven thickness of glass products and therefor the breakage at some weak points. While a glass gob is pressed in the blank mould for producing bottles, the distribution of stress is quite complex, which depends on the geometry of the mould and the place in the mould. At some sites, tensile stress dominates, whereas, at some sites, compression or shear stress dominates. The uneven distribution of the stress results in different extent of shear thinning of glass melt at different places of the mould, and vice versa. In addition, the conditions of heat transfer in bothe melt and mould during forming of melts could be influenced by an uneven shear thinning. Therefore, in future it is necessary numerically to simulate the distribution of the stress exerted to the glass melt during forming process, the shear thinning flow, the extensional thinning flow, the viscous heating flow and the heat transfer. Such a simulation is beneficial to a better design of the mould for forming and to an optimisation technological parameter of forming process. For an reasonable simulation, the difference of the extent of shear thinning at different positions of mould should be taken into a special consideration. To do so, a study of shear thinning behaviour is carried out in the present work.

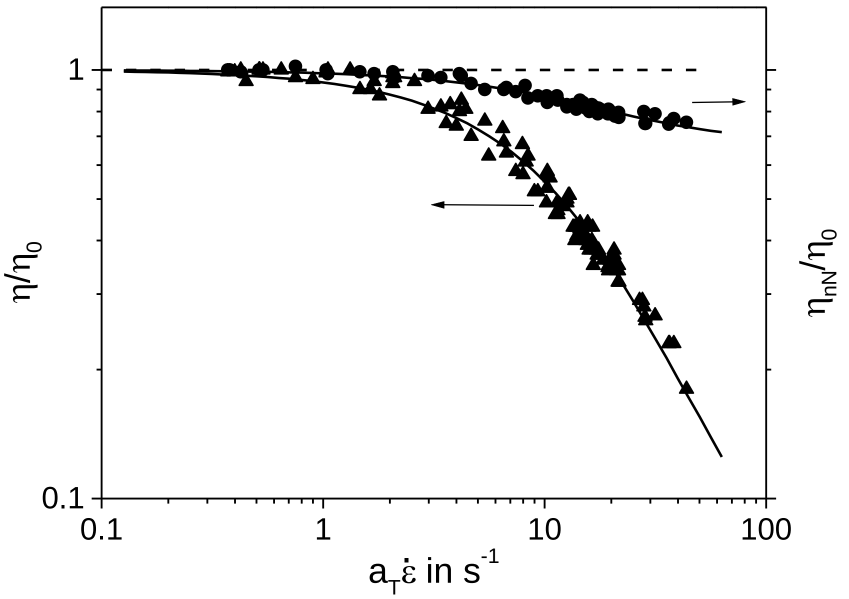

Fig 4. Master curves of the normalised non-Newtonian viscosity, (η_{nN}/η_0) , and the normalised actual viscosity, η/η_0, versus the normalised axial deformation rate, $a_T\dot{\varepsilon}$, for the glass melt 1 and 2 at a deformation degrees of $\Delta h/h_0$ = 15%. The curves were obtained using Eqs. (4) and (5), respectively.

Fig. 4 shows the dependence of the normalised viscosities, η/η_0 and η_{nN}/η_0, on the product of shift factor and deformation rate, $a_T\dot{\varepsilon}$, at different temperatures, where a_T is calculated from Eq. 6. The dependence was featured by a non-linear decrease of viscosity with increasing deformation rate. This is so-called shear thinning behaviour as mentioned above. However, the extent of the shear thinning is independent of temperature, as shown in Fig. 4, where the experimental data at different temperatures were overlapped. Therefore, it is possible to construct a master curve by using the shift factor, which is representative for all the temperatures above T_g. Master curves were also obtained from other glass systems studied in Refs. [1]. The existence of master curves again confirmed the conclusion that glass is a thermorheologically simple fluid, at least in the range of the temperatures of the experiments which had been done so far. The master curve provides a possibility to predict the shear thinning behaviour at such high temperatures at which it is difficult to carry out the measurements with the present cylinder compression method. At a viscosity lower than 10^6 Pa s, the cylindrical form of samples would easily be lost due to their own weight.

As shown in Fig. 4, the shear thinning behaviour of two melts could be represented by the solid curves obtained by fitting the measured data with Eqs. 1 and 2. The upper curve stands for the shear thinning effect only attributed to the orientation of flow units and the viscoslasticity of the glass melts. This effect is often termed the structurally Non-Newtonian flow. The lower curve represents the gross shear thinning behaviour consisting of the structurally non-Newtonian effect caused by orientation of structural units in the shear direction and the viscous heating effect attributed to dissipation of the heat produced by mechanical work. Obviously, the viscous heating effect plays a big role in initiating the shear thinning, in particular, at high shear rates. However, the existence of the structurally Non-Newtonian flow is verified by considering the viscous heating effect. From the practical point of view, the information on the trends of the change of both tensile strength and shear thinning behaviour with the deformation rate, shown in Figs. 3 and 4, is important for a good simulation and control of forming process, and a good design of the mould.

CONCLUSIONS

The fracture behaviour of high viscous melts is sensitive to a slight shift of the Newtonian viscosity - temperature relation. This shift is usually caused by a small fluctuation of the chemical composition of melt, which is again attributed to the instability of the production. The shear thinning effect of TV glass melts is pronounced, which is related to the two behaviours: the viscous heating and the structurally non-Newtonian flow related to the orientation of flow units and viscoslasticity of the glass melts. However, the former plays a bigger role in arousing the shear thinning than the latter. Master curves of shear thinning have been constructed by using a shift factor.

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